

# An Integrated Flame Spray Process for Low Cost Production of Battery Materials

***Yangchuan (Chad) Xing***  
*Department of Chemical Engineering*  
*University of Missouri*  
*Columbia, MO 65211*

*June 5-9, 2017*

**Project ID#: ES269**

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

# Overview

## Timeline

- Start: January 1, 2016
- End: December 31, 2018
- Work completed: 1<sup>st</sup> quarter

## Budget

- Total project funding
  - DOE share: \$2,215,556
  - Contractor share: \$310,694
- Funding received in FY 2016
  - \$516,607
- Funding for FY 2017
  - \$736,914

## Barriers

- Low cost target of \$125/kWh
- Sustainable materials manufacturing
- Energy density target of \$250 Wh/kg

## Partners

- University of Missouri – project lead
- EaglePicher Technologies

# Relevance

## Objectives

The overall objective of this project is to develop an advanced manufacturing technology for battery materials production at low cost and in a green chemical process. Specific objectives are:

1. To achieve a laboratory scale production rate of at least 3 kg/day of active battery materials using the integrated flame spray pyrolysis (iFSP) technology (by year 2),
2. To reduce active material cost by at least 25% to \$34/kg or less as compared to a baseline \$45/kg (by year 3), and
3. To develop a pilot scale production line with a manufacturing capacity of at least 4 metric tons of active battery materials per year (by the end of the project).

# Milestones

## Milestones for Budget Period 1 FY16/FY17 and Work Status

Milestones	Type	Description	Status	
			Planned	% completion
1.1	Tech	By the end of the first quarter (Q1), we will achieve a precursor DES formulation to make $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ .	03/31/2016	100
1.2	Tech	By the end of Q2, we will achieve a precursor DES formulation to make $\text{Li}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ .	06/30/2016	100
1.3	Tech	By the end of Q3, we will construct an operational flame spray pyrolysis reactor that can spray the DES precursors.	09/30/2016	100
1.4	GNG	By the end of Q4, we will demonstrate a production capacity of 1.5kg/day with the high throughput spray technology.	12/31/2016	100

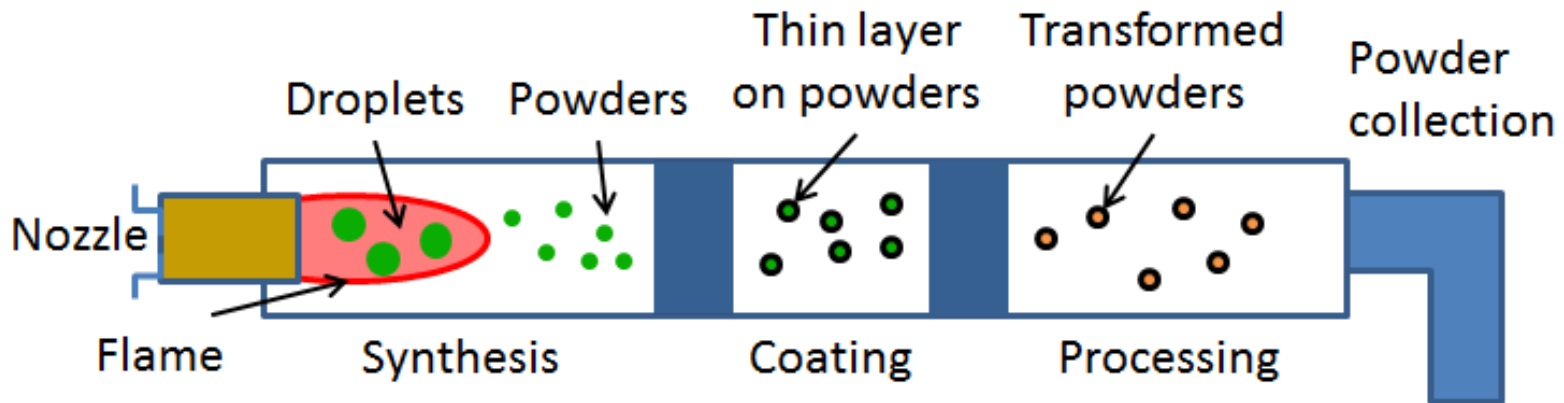
# Milestones

## Milestones for Budget Period 2 FY17/FY18 and Work Status

Milestones	Type	Description	Status	
			Planned	% completion
2.1	Tech	Demonstrate control of active material powder sizes to around 10 microns on average.	06/30/2017	75%
2.2	Tech	Select an in situ or semi-in situ coating process.	09/30/2017	15%
2.3	Tech	Cell design including matching anode and suitable electrolytes.	06/30/2017	25%
2.4	Tech	Demonstrate five (5) cells of 250Wh/kg energy density (at C/3 rate).	12/31/2017	-
2.5	GNG	Demonstrate a production capacity of 3 kg/day with the high throughput spray technology.	12/31/2017	-

# Approach

**The proposed manufacturing technology will integrate multiple processes into one to reduce cost.**



The battery powder production is aimed at integrating synthesis, coating, and processing into one process. In addition, biomass glycerol is used to replace water as solvent that would also save water treatment cost. This integrated process would significantly reduce the cost of the active materials production.

# Technical Accomplishments and Progress

## Deep eutectic solvent (DES) precursors

1. Deep eutectic solvent (DES) precursors have been successfully formulated and made. The primary solvent component is glycerol from biomass. This component forms DESs with many metal salts. In the project, acetates of the Li, Ni, Co, and Mn were selected and used to make the NMC materials. The work was focused on making the generally accepted material  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  with 1/3 of each of the transition metals. An optimized composition, *i.e.*, 1 molar of metals and 5 molar of glycerol, was achieved. This is the initial composition used to make NMC powders.
2. For NCA material, a formulation was also worked out. In this formulation, the DES contains aluminum nitrate as the Al source.

# Technical Accomplishments and Progress

## Spray nozzle design and reactor Gen 2.0

1. Spray nozzle design and flame reactor construction were accomplished and tested. To spray high viscosity DESs, an industrial nozzle with 1 gallon per hour capacity (of water) was used. This nozzle was further modified in order to accommodate spraying of the DES. Sprays from this improved nozzle have a significantly reduced droplet sizes and thus powder sizes.
2. A flame reactor was also constructed initially but an improved version of the reactor (Gen 2.0) was further constructed and used for making the NMC powders. The Gen 2.0 reactor was able to make spherical shape powders with little porosity.



# Technical Accomplishments and Progress

## NMC Powders: Characterization and Cell Test (1)

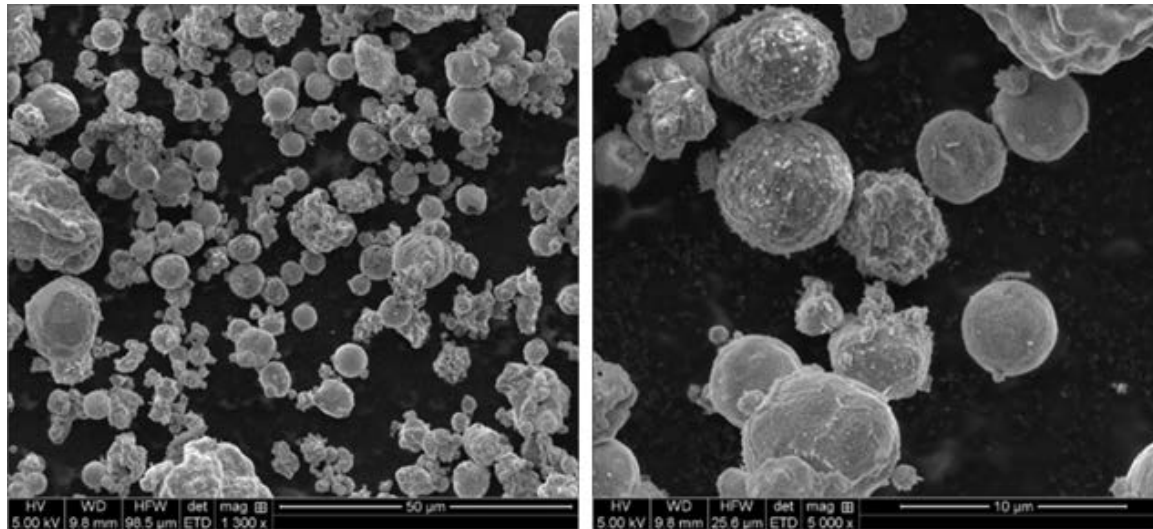
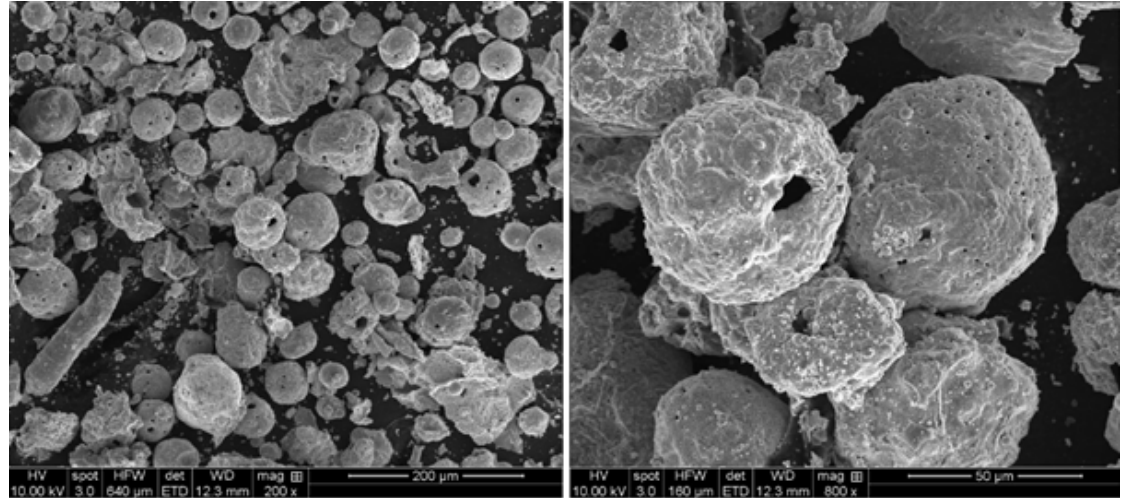
Materials characterizations and testing were accomplished. The produced NMC powders were characterized using advanced physical (SEM, XRD, EDS), and chemical analysis (ICP-MS) techniques.

1. Spherical powder morphologies were achieved, a significant improvement from the initial mostly flake morphologies. Improved powders are much less porous (see SEM images in the following slide).
2. It was observed that lithium loss occurred in the synthesis process, which is currently being addressed.
3. Coin cell tests were performed. Low capacity was observed, attributed mainly to the deficiency in lithium in the NMC material. A much higher capacity was achieved most recently by increasing Li content in the powders.

# Technical Accomplishments and Progress

## NMC Powders: Characterization and Cell Test (2)

The NMC powders produced in Gen 1.0 reactor, showing a size of ~50 microns. They are also porous.



Powders produced from the Gen 2.0 reactor, showing average size of 3 microns, much smaller than those obtained previously. The powders also appear to be solid, not porous as before.

# Technical Accomplishments and Progress

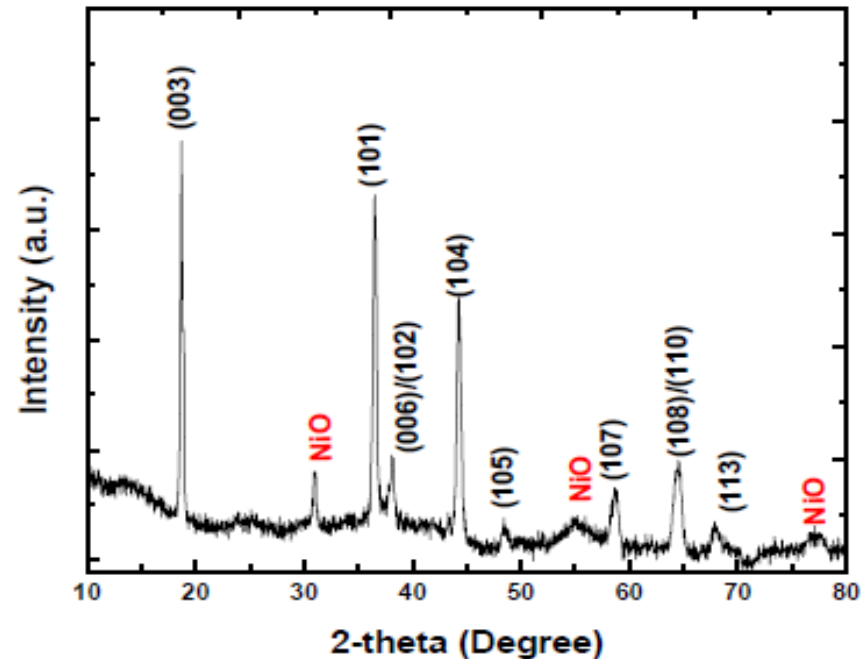
## NMC Powders: Characterization and Cell Test (3)

1. The elemental analysis indicated that the powders are deficient in Li, which lost about 21% in the pyrolysis synthesis process.

ICP-MS analysis results

Elements	Li	Mn	Co	Ni
Moles/Mole	0.791	0.346	0.320	0.334

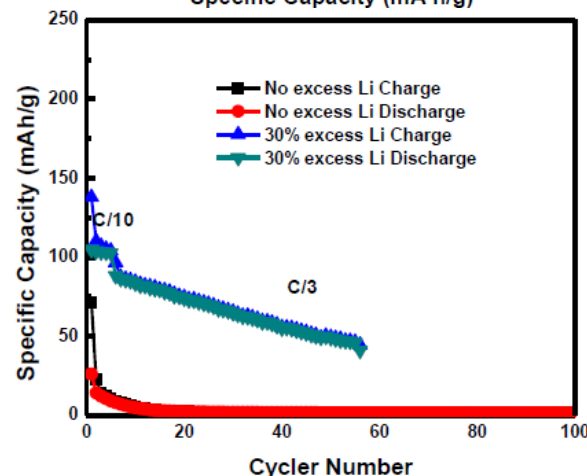
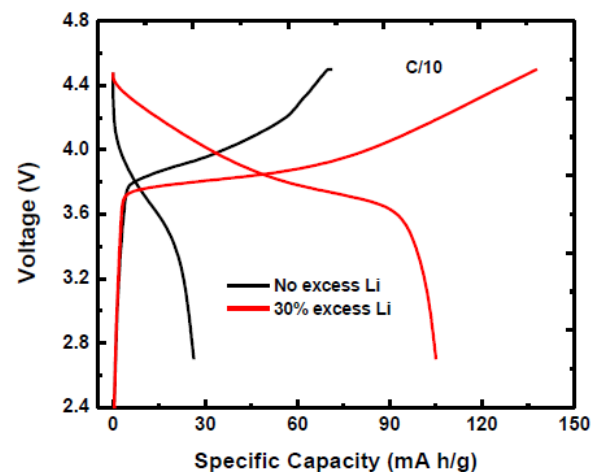
2. The powder structures are analyzed by XRD, which also indicated a deviation from NMC materials and an additional phase of NiO was observed. This was a result of Li deficiency.



# Technical Accomplishments and Progress

## NMC Powders: Characterization and Cell Test (4)

3. The powders were tested in coin cells with Li foil. The NMC powders produced from the original DES precursors showed very poor capacity, due to the 21% deficiency of Li in the powders.
4. Most recent effort was to compensate the Li loss during the synthesis, in which a 30% excess in Li precursor was prepared and used. As a result, the capacity is much improved.
5. The powders in tests have not been optimized. We expect further studies would significantly improve the capacity to reach the nominal capacity of the NMC material.



# Technical Accomplishments and Progress

## Powder production rates

1. High throughput was achieved and Go/No go target reached. The improved nozzle was able to spray the DES precursors at a high flow rate. The nozzle was able to spray 0.46 gallon per hour of the DES precursor, which would generate NMC powders of 5.47 kg/day.
2. Powders of 1.63 kg/day were actually achieved in a preliminary powder collector, exceeding the Go/No Go target of 1.5 kg/day.
3. Significant improvement on the powder collection efficiency is expected in current effort, in which a new powder collection system is being constructed to achieve the BP2 target of 3.0 kg/day production rate. The new reactor of Gen 3.0 has also been constructed to achieve the production rate.

# Responses to Reviewers' Comments

As a new project last year only three months into the work, the reviewers were mostly positive about the work, but have reservations about the outcomes from the project.

Reviewer 4 in Q1, **comment**: “The reviewer’s concern is that the PI has no intention at present to compare their future findings to what could be produced using water with the same raw materials.”

**- Response**: (1) in terms of cost, it will be compared in cost analysis to the water based production, which will be used as benchmark. (2) in terms of performance, we will compare it with water-based co-precipitation method. This will be done in the 3<sup>rd</sup> quarter of this year’s effort.

Reviewer 5 in Q1, **comment**: “while the team claims the process can significantly reduce the cost, there is no cost analysis to show how much the cost reduction might be.”

**- Response**: Our initial cost analysis in the original proposal was based on the fact that integrated processes save significantly than individual processes. And it is possible to cut active materials cost by 25%. However, this cost analysis has to be re-evaluated based on future development. While this is not a milestone in the project, it will be done as the cost reduction has to be justified. This will be done in budget period 3 with collaborations with partners.

# Responses to Reviewers' Comments

Reviewer 2 in Q2, **comment**: “much progress has been made within three months, and that the process apparently needs further optimization.”

**- Response**: Indeed, optimization has been a major effort over this last year, as we have tried to optimize the powder morphology by optimizing the process, and in the meantime to achieve the production rate go/no go target. System optimization will be an continued effort in this year in which powder morphology optimization and process control will be studied.

# Collaborations

1. EaglePicher Technologies as a partner has been conducting tests of the materials in their battery cells with a proprietary anode. Cell test and optimization will be the main work in this budget year.
2. Future collaborations will be forged to look at the process cost. A cost model will be developed based on the new process, which will be compared to co-precipitation method. Potential partners include National Labs or companies working in process cost analysis.



# Remaining Challenges and Barriers

1. Production rate will continue to be a challenge but will be achieved during this year's effort. A Gen 3.0 reactor is being tested.
2. Morphology control, especially during process scale up, poses a challenge. As the production rate is increased, the nozzle capacity will also have to be increased, directly related to droplet sizes. This will be optimized in future studies.
3. The low capacity of the prepared NMC materials needs to be increased. The NMC materials tested have not been optimized, and showed an deficiency in lithium and a low capacity. Lithium loss during synthesis will be a challenge.

# Proposed Future Research

1. To optimize the nozzle to produce powders with desired characteristics.
2. To improve on the Gen 3.0 reactor to produce powders at the targeted production rate, while achieving the powder morphology.
3. To control conditions to achieve powder morphologies, with spherical size at 10 microns and dense powders.
4. To continue to improve the DES precursors to synthesize NMC powders with stoichiometric ratios and much increased capacity.
5. To design and optimize battery cells.
6. To design and integrate processes.

Any proposed future work is subject to change based on funding levels.

# Summary

1. This project is to develop a manufacturing technology for low cost production of active materials for Li-ion battery.
2. Over the first year, we have achieved all scheduled milestones and go/no go target.
3. A Gen 3.0 reactor has been constructed. We expect to achieve the production rate target of this year, as well as cell performance using optimized active materials.
4. We have achieved significant improvements in the past year in powder morphology and active materials capacity. We will continue to improve them to reach the targets.
5. The experiences accumulated in the first year will help us further improve the manufacturing process and take it to the next level.